THEORETICAL ESTIMATES OF REACTION OBSERVABLES VIS-A-VIS MODERN EXPERIMENTS

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1 Abstract

Recent advances in experimental chemical reaction dynamics are examined. The paper focuses on crossed beam technologies because the detailed single collision information they provide is a stringent test of the adopted molecular interaction. In this respect some prototypal atom-diatom and diatom-diatom elementary reactions are analysed.

2 Introduction

Modern understanding of chemical reactive processes is based on the assemblage of a suitable potential energy surface (PES) out of the first principles (*ab initio*) calculations of electronic energies and on the integration (on the adopted PES) of the equation of motions of the nuclei. In this respect theoretical and computational machineries have made impressive progress and it is now possible to compute rigorously using *a priori* techniques several averaged as well as highly detailed properties of gas phase reactions (see the preceeding lecture (1) and references therein).

This is indeed a clear example of synergistic development of theory and experiment. As a matter of fact, the traditional quantity to measure for chemical reactions used to be the concentration (of either the reactants or the products) as a function of the time elapsed from the starting of the process while keeping under control temperature and pressure. Concentrations can be easily measured for processes occurring on the time-scale of minutes or longer (this is the case of the popular thermostated vessels, discharge flow, flash photolysis, shock wave, etc. measurements). For shorter time-scales this technique is impractical unless the determination of the concentration (or even the starting of the process) is reconducted to the determination of fast to measure physical properties of the system (like some spectroscopic ones). Moreover, from bulb experiments no information can be obtained on the intervening individual state-to-state elementary uni and bi-molecular processes.

Such an information can be obtained, instead, from Crossed Molecular Beams (CMB) experiments. As a matter of fact, the measurement of the efficiency of fast bi-molecular reactions has become possible in the mid fifties (of the 20th century) when Datz and Taylor (2) carried out the first CMB experiment of the K + HBr → KBr + H reaction. The distinct innovative feature of CMB experiments that marked the birth of the experimental molecular dynamics, is the possibility of working in a single-collision regime. The conceptual foundations of molecular dynamics date back to the advent (in the twenties) of quantum mechanics. Quantum mechanics studies prompted, in fact, the request for investigating the collision processes in beams and their outcomes. Theoretical studies of atomic and molecular collisions are usually articulated in a first step devoted to the calculation of electronic energies (for which separate accurate *ab initio* computational procedures are available) and a second step integrating the equations of motion of the nuclei on the PES associated with the electronic energies calculated in the first step considered (for which software is less standard). As a matter of fact, this has led to the construction of the first semiempirical PES (3) for the H + H_2 reaction, to the extension of the theoretical investigation to other systems of chemical interest (4) and to the conduction, as well, of the first classical trajectory (QCT) computational study of reaction dynamics (5).
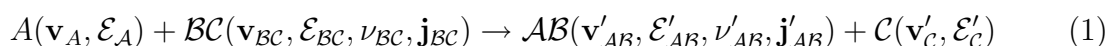
The real breakthrough of molecular reaction dynamics, however, has occurred in the sixties. As to theory, in fact, significant improvements were made by the early 1960s in calculating both *ab initio* and semiempirical PESs as well as in integrating classical trajectories for the full three-dimensional treatment of atom-diatom reactions (6). As to the experiment, in the sixties the first experiments measuring product angular and translational energy distributions for a large variety of alkali atom reactions (7; 8) were performed. During the same period, the infrared-chemiluminescence technique (9) was developed which allowed the determination of nascent product vibrational-rotational distributions for many halogen and hydrogen atom reactions. Finally, at the end of the '60s, the first universal CMB apparatus was built. The universal CMB machines are characterized by the fact of having supersonic beam sources for the reagents and an electron impact mass spectrometer detector (10) and a pseudo-random time-of-flight (TOF) velocity analyser for the products. This allows the universal CMB machine to measure not only the integral (over the angular range) cross section (ICS) but also the differential (DCS) one. This has opened the field to other experimental innovations (see for an introduction to the field the books (12; 13) as a general review and for focus on some specific aspects see the papers (8; 14; 15; 16)). More recent reviews are given in refs. (17; 18; 19; 20; 21; 22; 23; 24; 25; 26; 27; 28; 29; 30; 31; 32; 33; 34; 35; 36; 37; 38; 39; 40; 41) with the latter being the main source of experimental information for the present paper.

The paper is articulated into the following sections: section 2 illustrates the modern evolution of crossed molecular beams as a universal tool for investigating bi-molecular processes; section 3 discusses the case of few atom systems to analyses the interaction between experimental and theoretical studies.

3 The universal CMB

As already mentioned the advent of the universal CMB machine has profoundly innovated the field of reaction dynamics (as testified also by the award of the 1986 Nobel Prize to three top researchers of the field). The universal CMB has, in fact, made it possible to investigate a large variety of elementary reactions. As an example, during the 1970s and early 1980s several reactions involving hydrogen, oxygen and halogen atoms, were investigated in detail using universal CMB apparatuses (15; 42). The distinctive feature of CMB techniques, due to the use of ultra-high-vacuum (UHV) technologies, is the possibility of dealing specifically with all the parameters of an elementary reactive process.

Experiments performed on universal CMB machines, in fact, can measure the laboratory (*lab*) fixed angle ($I_{lab}(\theta', u')$) flux intensity of products (by convention primed quantities refer to products) as a function of θ' (the angle of deviation of the recoil direction from the original one) and u' (the speed of the recoiled flux) starting from reagents in well defined states for virtually any reaction (11). However, theoretical treatments work on the center-of-mass (*cm*) reference frame. This means that, for example, the simplest bi-molecular elementary reactive process *i.e.* the atom-diatom reaction that can be schematized as:

$$A(\mathbf{v}_A, \mathcal{E}_A) + \mathcal{BC}(\mathbf{v}_{\mathcal{BC}}, \mathcal{E}_{\mathcal{BC}}, \nu_{\mathcal{BC}}, \mathbf{j}_{\mathcal{BC}}) \rightarrow \mathcal{AB}(\mathbf{v}'_{\mathcal{AB}}, \mathcal{E}'_{\mathcal{AB}}, \nu'_{\mathcal{AB}}, \mathbf{j}'_{\mathcal{AB}}) + \mathcal{C}(\mathbf{v}'_{\mathcal{C}}, \mathcal{E}'_{\mathcal{C}}) \quad (1)$$

in which reactants and products are characterized by the speed v, the angle Θ, and a set of internal (electronic $\mathcal{E}$, vibrational ν, and rotational j) quantum states (primed quantities

are for products, unprimed for reactants). For CMB experiments several techniques have been developed to generate the reactants in specific quantum states and with a narrow velocity distribution as well as to detect the velocity, angular and in internal quantum states of the products.

3.1   The reactant beam generation

The first key feature of a CMB experiment is the production of sufficiently intense continuous or pulsed beams of reactants with a sufficiently narrow velocity distribution. At first the problem was tackled by mechanically selecting effusive beams. More recently the problem has been addressed by generating supersonic beams. Supersonic beams have a higher intensity, a narrower velocity spread and are generated by expanding a high-pressure gas through a nozzle into a high-vacuum chamber (43). This is particularly difficult for unstable reactants like atoms and radicals. However, the progress made in dealing with pulsed lasers and seeded beam techniques has allowed the generation of supersonic beams of virtually any atomic species and of a large variety of radicals (*e.g.* continuous and pulsed beams of N, C and of several diatomic radicals like OH and CN). It has also allowed to generate pulsed beams of polyatomic free radicals allowing the study of reactions of combustion-, atmospheric-, and astro-chemistry interest. The main methods used to generate beams of transient reactants (atoms or molecular radicals) are similar to those used in bulb studies, i.e., pyrolysis, photolysis, or discharge of a suitable precursor (eventually to be followed by a chemical reaction inside the nozzle).

3.1.1   The beam specificity

Intensity, purity, and cooling are the three main factors which come into play when one desires to generate a beam of highly specific characteristics. High beam intensity is, of course, a prerequisite for reactive scattering, to guarantee a detectable quantity of final products. Purity is also a key issue to uniquely identify the detailed outcome of elementary processes. Mixtures of species, however, and in particular mixtures of different electronic states of the same species have been in various occasions exploited to study the dependence of the cross section on the internal energy especially when one can play with the percentual composition. Efficient cooling, or state selection, is of concern mainly in state-to-state studies. Radical beams, when generated in a supersonic expansion, usually attain a high degree of state selection, albeit restricted to the lowest rotational levels. However, if the radical is initially created in highly excited states, for instance by photolysis or high temperature pyrolysis, the cooling to the lowest ro-vibronic levels may not be very efficient.

Further specificity of the reactants is obtained through the control of the orientation and alignment of reagents using exapole state-selection, brute force (by magnetic or electric fields) alignment or orientation, and polarised laser radiation methods. These methods have enabled the investigation of stereodynamical aspects of chemical reactions at a fundamental level. Advances were also made in photo-initiated reactions, real-time studies (femtochemistry) and transition state spectroscopy experiments. In more recent years CMB methods have been extended to the generation and study of a large variety of atoms, molecules and radicals of increasing complexity including biological systems with

a consequent shift of the research focus from fundamental to more applicative scopes.

3.1.2 Continuous and pulsed supersonic beams of transient species

Supersonic beams of metal atoms seeded in a carrier gas are usually generated continuously in a high temperature oven (alkali, alkali earth) (26; 44) or by pulsed laser ablation (Mg, Al, C, Si, and transition metals such as Ti, V, Cr, Cu, Y, Zr, Mo) (45; 46). This source has also been successfully adapted to a universal CMB apparatus to measure reactive DCSs for a large series of reactions with unsaturated hydrocarbons, of particular relevance to astrochemistry and combustion. Other minor products of these generation methods have also been used as reactant beams. Supersonic continuous beams of non-metal atoms were produced traditionally by pyrolysis and/or electrical discharge (micro-wave or radio-frequency), starting from dilute mixtures of the stable molecules in a rare gas. Continuous N-atom and C-atom (47) beams both in the ground and the first electronically excited state, sufficiently intense to allow measurements of DCS, have been produced using the same radio frequency discarge built for O atom beams. Intense beams have been produced also for D, O, S, Cl and F radicals either by pulsed laser photolysis or by pulsed discharge.

As to molecular radicals, important advances have been made in the generation of continuous beams of OH and pulsed beams of CN. Beams of C_3H_3 have been obtained by laser photolysis of C_3H_3Br (48) and CN (49) by laser ablating carbon atom from graphite in the presence of N_2. Beams of C_6H_5 and C_2D have also been produced for use in CMB experiments. A pulsed fully state-selected beam of OH($X^2\Pi_{3/2}$, $j = 3/2$, Λ) radicals has been generated using a pulsed electrical discharge with hexapole selection. More intense beams of jet-cooled molecular radicals (OH, CH_3) have been obtained by combining slit supersonic expansion and pulsed electrical discharges (50).

3.1.3 Reagent state-selection

Most of the beam sources allow a selection of the reactants collision energy and have been used to determine the translational energy dependence of DCSs and ICSs (the dependence of ICS from the collision energy is often called also "excitation function"). Translational energy can be varied using rotating velocity selectors, changing the nozzle temperatures and exploiting the seeding effect in a (rare gas) carrier gas. TOF selection of one reagent has also been used in beam-cell experiments (16). Accurate excitation functions have been obtained by using crossed pulsed beam apparatuses with independently rotating beam sources, which make it possible to vary the translational energy down to very low values by simply varying the crossing angle of the two beams (17; 43; 51). This has allowed, for example, accurate measurements of the excitation function for the reactions O(^{1}D), S(^{1}D), Cl(^{2}P), F(^{2}P), and CN + H_2(D_2, HD) (52; 53; 54; 55; 56; 57) and for the reactions C(^{3}P)+O_2 and C(^{3}P)+NO, C_2H_4 (51).

An efficient way of preparing the reagent molecules in the lowest rotational states is through the cooling which occurs during the expansion of the supersonic beam. The preparation of H_2 and D_2 beams in the ground $j = 0$ rotational level has been obtained via a catalytic conversion to p-H_2 or o-D_2. The production of rotationally excited HCl(ν=2, j=1, 6, 9) with O(^{3}P) and O(^{1}D) (54; 58) has allowed the study of the effect of rotational excitation on the product energy disposal.

To study the effect of vibrational energy on the DCS one can use laser radiation to selectively excite vibrational modes (usually of stable molecules). An example of CMB measurements of DCSs for a rovibrationally excited reagent is represented by the studies of Li, K, Sr + HF(v=1, j=1, m=0) reactions (26). Highly detailed studies of selective vibrational excitation have been carried out using the pump-probe and photo-initiation methods (33; 59; 60).

Electronic and spin-orbit excitation have been mainly studied for atoms. The effect of electronic excitation on chemical reactivity and dynamics is quite distinct because through electronic excitation strongly endoergic (inefficient) reactions may become very efficient. The effects of electronic excitation on ICS (especially of metal atoms) and on DCS have been investigated by generating short-lived electronically excited alkali (Li, Na, K, Cs) (61; 62), alkali earth (Ca, Sr, Ba) (44) and transition metals (V, Mo) (63). Electronic excitation of Ca atoms has also been generated by DC discharge (31) while that of the O, S, N and C non metal atoms has been obtained by RF discharge (O^{1}D), N(^{2}D), C(^{1}D)) (23; 64; 65) and by laser photolysis of a suitable precursor molecule. These species have long lifetimes and can be generated well before the collision region. Spin-orbit effects and differences in branching ratios for spin-orbit states of product atoms are also observed in chemical reactions by measuring both quenching rates and chemiluminescent yields (see (66; 67; 68)).

3.2 The product detection and characterization

In addition to the possibility of measuring the speed and the direction of reactants, the other key feature of a CMB experiment is the possibility of measuring the speed and the angular distributions of the products (or, when is the case, the angular distributions of the state-selected products and their orientation or alignment). To this end several technologies have been developed to deal with the low density of scattered products. In the '70s the Laser-Induced-Fluorescence (LIF) technique was adopted (69). Advances were also made in the detection of products using photo-ionization by tunable synchrotron or VUV laser radiation, CARS (Coherent-AntiStokes-Raman-Spectroscopy), infrared absorption, and REMPI (Resonance-Enhanced-Multiphoton-Ionization). Alternative and complementary techniques were implemented for determining reactive integral and differential cross sections like ion-imaging, Doppler methods and the H-Rydberg atom TOF spectroscopy. In addition, advances in the probing of the orientation of the products, by exapole state-selection, by brute force, and by polarised laser radiation methods have enabled the investigation of stereodynamical aspects of chemical reactions at a fundamental level.

3.2.1 Rotatable mass spectrometry

The main detection device able to measure $I_{lab}(\theta', u')$ at different values of θ' is the universal rotatable electron impact mass spectrometer. Rotatable detectors are usually made of an (electron-impact or photo) ionizer, a quadrupole or magnetic sector mass filter, and an ion counting device, such as a Daly detector or a secondary electron multiplier mounted on a UHV chamber that can rotate around the collision region (10). In this way one can plot the speed of the atomic or molecular products as a function of the scattering angle.

The contour maps of the speed flux of the reaction products can be regarded as an image of the reaction in angle-velocity space. The kinetic energy distribution of one of the products of a bimolecular reaction measured by TOF spectroscopy provides also information about the undetected product through conservation of energy and linear momentum (70). UHV conditions are mandatory in the ionization and detection zones to measure fluxes as low as 10^4 molecules cm^{-2} s^{-1}. This requires a special care in choosing materials, drawing mechanical design, adopting UHV pumping (including differential pumping) techniques. A detector of this type must have a reduced size and weight to be housed in a UHV chamber rotated both in and out the plane. Optical detection can provide an alternative (in favorable cases) to mass/TOF spectroscopy detection.

3.2.2 Photoionization

Electron-impact ionization has, however, some disadvantages like dissociative ionization of the neutral reaction product (this is the most serious problem because fragmentation in the ionizer can complicate the identification of reaction products especially when several reaction channels are open at the same time), the high background partial pressure produced by the hot filament used in the electron-impact source especially for H, H_2, CH_4, H_2O, CO, CO_2, energy and time limitations to the resolution induced by space-charge effects. To the end of improving the signal-to-noise ratio magnetically suspended turbomolecular pumps and efficient cryopumping (down to 10 K) of the electron-impact ionization region have been introduced (71). To overcome the disadvantages associated with the electron impact ionization method photo-ionisation with tunable radiation techniques have been adopted. Dissociative ionization can be avoided by tuning the radiation below the dissociative ionization potential of a molecule or radical, and so detection of a species of mass m at the parent m/e mass ratio is possible. The residual background at critical masses can be kept to a minimum because of the negligible amount of heat generated. The tunability of the radiation adds selectivity in the internal energy of the detected species, in addition to universality. Further, no space charge effects accompany the process, so by spatially focusing the photons it is possible to attain high time-resolution for TOF measurements. The low ionization efficiency problem of this technique has been recently solved using synchrotron radiation sources (72), although applications to reactive scattering have been very limited, so far, for sensitivity reasons. Photoionization detection using commercially available laser sources has also been reported

3.2.3 Laser spectroscopic detection

In CMB experiments two main spectroscopic schemes have been applied for product detection: LIF and REMPI (recently, also, direct IR absorption has been used). The great advantage of LIF and REMPI techniques is that they are both state-specific and sensitive. Probing the reaction products at the collision region, has permitted the derivation of ICSs for many elementary reactions. The main limitation of these two techniques is their lack of generality. The availability of the proper light source is less of a problem nowadays than the detailed knowledge of the spectroscopy of the molecule or radical to be probed (detection of atomic products is usually straightforward). Predissociation in LIF, and the availability of suitable schemes in REMPI, in addition to the properties of the available tunable light sources, in practice restrict LIF and REMPI detection to small radicals and

molecules (35). Furthermore, probing the entire ro-vibrational distribution of a reaction product is often difficult, if several vibrational levels are populated. Nevertheless, the amount of detail obtained from these state-specific detection schemes is impressive, and they have played an important role in the development of reaction dynamics during the '80s and '90s. Laser probing at the collision region, exploiting ion-imaging techniques or Doppler profiles, represent an alternative as well as a complementary approach to the CMB method with rotating detector and TOF analysis for measuring reactive DCS.

3.2.4 Ion-imaging and Doppler methods

Imaging techniques are an alternative modern approach to the simultaneous, in principle state specific, measurement of angular and velocity distributions of reaction products (73). Full three-dimensional velocity distributions can be recovered from the analysis of the ion images. Using this technique some vibrational resolution was achieved (74). Recently, the resolution of the ion-imaging method has been dramatically improved with the introduction of the velocity mapping scheme (75; 76).

The technique of measuring state-resolved DCS by Doppler spectroscopy following optical detection at the collision region by LIF of the scattered product was introduced by Kinsey (77). An interesting feature of this technique is that LIF probe with sub-Doppler resolution leaves encoded in the absorption spectral lines the angle-resolved velocity distributions of the state resolved product. Unfortunately, resolution and sensitivity problems due to low velocities and intrinsically lower signal levels do not allow a widespread application of Doppler techniques to reactive scattering though significant advances have been made (28; 62; 78).

A significant step ahead in the development of methods for measuring double DCSs is represented by the Doppler-selected TOF technique implemented by Liu and coworkers, and used to map out the three-dimensional velocity distribution of a reaction product, directly in the center-of-mass system. This technique combines the conventional Doppler-shift and ion TOF in an innovative manner, such that the net performance becomes more than additively enhanced.

4   Some case studies

In order to compare experiments with calculations and carry out their physical interpretation, one needs to express the measured $I_{lab}(\theta', u')$ in the cm coordinates Θ' and v' via the relationship

$$I_{lab}(\theta', u') = \sum_i f(E_{tr}) f_i(u_{r1}, u_{r2}, \gamma) \frac{u'^2}{v'^2} I_{cm}(\Theta', v_i'). \tag{2}$$

In eq. 2 $f(E_{tr})$ is the function expressing the dependence of the cross section from the collision energy E_{tr} and $f_i(u_{r1}, u_{r2}, \gamma)$ is the weight of the ith Newton diagram (the composition diagram of the velocities of the bi-molecular collision partners under the conservation laws of closed systems (79)) depending on the velocities of reagents $r1$ and $r2$ and the related collision angle γ. Then for any given set of reactant initial parameters (including when is the case orientation and alignment) which for sake of simplicity have

been dropped from the notation, the value of the center of mass flux $I_{cm}(\Theta', v')$ the product flux is formulated in terms of its energy dependent analogous as follows

$$I_{cm}(\Theta', v') = \frac{\mathrm{d}E'}{\mathrm{d}u'} I_{cm}(\Theta', E') = \frac{\int_o^\infty I_{cm}(\Theta', E')\mathrm{d}E'}{\int_o^\infty v' I_{cm}(\Theta', E')\mathrm{d}v'} I_{cm}(\Theta', E') \tag{3}$$

Then $I_{cm}(\Theta', v')$ is linked to the differential cross section $\sigma(\Theta', E'_{tr})$ (that can be directly obtained by a proper combination of the elements of the scattering **S** matrix of the theory see ref. (1) and form which the integral cross section $\sigma(E'_{tr})$ can be derived by integrating over Θ') using the relationship

$$I_{cm}(\Theta', E') = n_{r1} n_{r2} u_{tr} \sigma(\Theta', E') \Delta V J(\Theta') F \Delta\Omega' \tag{4}$$

where n_{r1} and n_{r2} are the densities of the first and second reagent, respectively, u_{tr} is the relative collision velocity of the reactant species, $\sigma(\Theta', E')$ is the differential cm cross section for the given initial state (or distribution of initial states) whose labels have been, however, dropped, ΔV is the collision volume, $J(\Theta)$ is the Jacobian of the $cm \to lab$ transformation, F is the detection efficiency, $\Delta\Omega'$ is the detection solid angle.

However, eq. 4 cannot be inverted and different sets of cross section values may satisfy equation 4 and ultimately the measured scattering data. For this reason the problem is usually tackled using forward convolution techniques. This means that cm angular and velocity distributions are given a functional representation whose parameters are varied to best fit the measured laboratory distributions (obviously, in doing so one has to take into account the velocity spread of the beams and the resolution of the TOF (that is the ratio between the length of the ionization zone and that of the flight length)).

4.1 The atom-diatom reactions

Atom-diatoms are the systems which have attracted most of the work comparing the results of theoretical and experimental investigations from the very beginning of CMB studies. In particular for atom-diatom systems some examples of comparison of state averaged, state resolved and state-to-state experimental ICSs and DCSs with both QM and QCT estimates are given in the literature. As a matter of fact, as already mentioned, the comparison of dynamical calculations with CMB data is, indeed, the most important probe of the accuracy of a proposed PES. The rigorous QM approach, however, becomes progressively heavier as the mass of the system and the structure of the PES increases. In fact, one needs to achieve convergence of the calculated cross sections with the value of the total angular momentum quantum number and with the size of the basis set (or grid points). For QCT calculations there are fewer difficulties in achieving convergence because it depends only on the number of trajectories integrated. Moreover, while trajectories are independent computational tasks which can be efficiently distributed for calculation on the grid (80), this is not so for QM calculations.

4.1.1 The H + H$_2$ reaction

The hydrogen exchange reaction H + H$_2$ → H$_2$ + H is the lightest and simplest neutral particles reaction. This reaction has been extensively studied, both theoretically and

experimentally, since the 1930s (see refs. (81; 82) for a review of older work). As a matter of fact the first accurate calculation of an *ab initio* PES (LSTH) (83; 84) and the first quantum (QM) calculation of reactive scattering properties (85) were carried out for H+H$_2$. More recently, it has become possible to make an accurate comparison between experiment and theory.

On the experimental side product-state and angular distributions have been measured (82; 86; 87) and DCS have been determined using the photoloc technique for H + D$_2$ leading to HD(ν=1, j=1,5,8) + D at E$_{tr}$=1.7 eV and to HD(ν=2, j=0,3,5) at E$_{tr}$=1.5 eV (88; 89). Extensive and detailed top CMB experiments were carried out by Welge and co-workers (74; 90; 91; 92; 93; 94). In these experiments state-to-state (rotationally resolved) DCS for the reaction H + D$_2$(ν=0,j=0) $\rightarrow$ HD(ν', j') + D were measured for a wide range of collision energies (from 0.53 eV up to 2.67 eV) using the ultra-high-resolution H-Rydberg atom TOF spectroscopy method. These results are the most comprehensive and accurate experimental data ever measured for a chemical reaction and have enabled a very detailed assessment of the quantum mechanical treatment of chemical elementary reactions.

The above listed properties of the H + H$_2$ reaction have been the subject of detailed comparisons with both QCT and QM scattering calculations (74; 95). In particular, state-to-state DCS at collision energies of 0.52, 0.531 and 0.54 eV have been compared with converged QM scattering calculations on the different *ab initio* PESs available from the literature for this system. This has allowed a direct assessment of their quality (96). Differences found in the QM calculations were traced back to slight differences in the topology (barrier height and bending potential) of the different PESs used in the calculations. The comparison showed that BKMP2 (97) is at present the PES most suitable to describe the reactive scattering process at low collision energy. At the higher value of E$_{tr}$=1.29 eV, the older and more popular LSTH PES still provides a good description of the experimental state-to-state DCS. A comparison of QM and QCT (though performed only on the BKMP2 PES) calculations showed that quasiclassical methods do a good job in reproducing the experimental results, except for the low collision energy rotationally state-to-state DCSs (98).

	Table 1	H + H$_2$ LSTH REACTIVE		$T=$ 300 K		
v'	v	1	3	5	7	9	11
0		.329(-13)	.248(-11)	.592(-11)	.587(-11)	.453(-11)	.156(-11)
1		.118(-12)	.289(-11)	.814(-11)	.762(-11)	.471(-11)	.339(-11)
2			.638(-11)	.110(-10)	.957(-11)	.708(-11)	.409(-11)
3			.560(-11)	.177(-10)	.140(-10)	.107(-10)	.579(-11)
4				.327(-10)	.244(-10)	.160(-10)	.858(-11)
5				.289(-10)	.396(-10)	.228(-10)	.131(-10)
6					.685(-10)	.397(-10)	.214(-10)
7					.592(-10)	.648(-10)	.292(-10)
8					.285(-13)	.112(-09)	.551(-10)
9						.997(-10)	.964(-10)
10						.887(-13)	.184(-09)
11							.168(-09)
12							.958(-12)

Table 2			H + H_2 LSTH REACTIVE		$T=$ 500 K	
v'	v	1	3	5	7	9	11
0		.684(-12)	.568(-11)	.993(-11)	.109(-10)	.726(-11)	.359(-11)
1		.992(-12)	.775(-11)	.119(-10)	.115(-10)	.710(-11)	.527(-11)
2			.148(-10)	.181(-10)	.174(-10)	.109(-10)	.586(-11)
3			.150(-10)	.305(-10)	.234(-10)	.150(-10)	.966(-11)
4			.670(-14)	.529(-10)	.418(-10)	.243(-10)	.129(-10)
5				.473(-10)	.581(-10)	.364(-10)	.211(-10)
6				.984(-13)	.100(-09)	.575(-10)	.329(-10)
7					.847(-10)	.941(-10)	.500(-10)
8					.535(-12)	.162(-09)	.865(-10)
9						.126(-09)	.144(-09)
10						.208(-11)	.240(-09)
11							.199(-09)
12							.111(-10)
13							.360(-12)

Table 3			H + H_2 LSTH REACTIVE		$T=$1000 K	
v'	v	1	3	5	7	9	11
0		.472(-11)	.152(-10)	.190(-10)	.152(-10)	.130(-10)	.551(-11)
1		.852(-11)	.186(-10)	.226(-10)	.219(-10)	.131(-10)	.762(-11)
2		.248(-12)	.400(-10)	.312(-10)	.270(-10)	.190(-10)	.129(-10)
3			.408(-10)	.567(-10)	.411(-10)	.291(-10)	.164(-10)
4			.123(-11)	.970(-10)	.642(-10)	.466(-10)	.233(-10)
5				.846(-10)	.102(-09)	.629(-10)	.418(-10)
6				.342(-11)	.153(-09)	.103(-09)	.623(-10)
7				.887(-13)	.131(-09)	.155(-09)	.846(-10)
8					.760(-11)	.198(-09)	.144(-09)
9					.295(-12)	.177(-09)	.221(-09)
10						.204(-10)	.290(-09)
11						.197(-11)	.250(-09)
12						.792(-13)	.514(-10)
13						.930(-14)	.752(-11)
14							.371(-12)

These conclusions encouraged us to carry out an extensive campaign of rate coefficients calculations for the H + H_2 reaction by running trajectory calculations on the LSTH PES.

Calculated rate coefficients for reactive transitions are reported in the tables 1 - 5 for increasing values of the temperature T. In the tables values of the rate coefficients are given in units of 10^xcm^{3}molec^{-1}s^{-1} with x being given in the round brackets. Initial vibrational states ν are given in the first row while final states ν' are reported in the first column.

v'\v	1	3	5	7	9	11
0	.237(-10)	.279(-10)	.334(-10)	.286(-10)	.211(-10)	.973(-11)
1	.403(-10)	.465(-10)	.436(-10)	.339(-10)	.272(-10)	.126(-10)
2	.433(-11)	.853(-10)	.633(-10)	.510(-10)	.374(-10)	.217(-10)
3	.265(-12)	.912(-10)	.102(-09)	.759(-10)	.572(-10)	.332(-10)
4	.888(-14)	.136(-10)	.162(-09)	.114(-09)	.775(-10)	.446(-10)
5		.131(-11)	.132(-09)	.163(-09)	.117(-09)	.645(-10)
6		.112(-12)	.252(-10)	.209(-09)	.159(-09)	.963(-10)
7		.191(-13)	.320(-11)	.166(-09)	.225(-09)	.142(-09)
8			.273(-12)	.492(-10)	.271(-09)	.199(-09)
9			.197(-12)	.922(-11)	.196(-09)	.257(-09)
10				.150(-11)	.728(-10)	.299(-09)
11				.242(-12)	.202(-10)	.259(-09)
12				.554(-13)	.424(-11)	.900(-10)
13				.167(-13)	.935(-12)	.242(-10)
14					.729(-13)	.275(-11)

Table 4   H + H_2 LSTH REACTIVE T=2000 K

v'\v	1	3	5	7	9	11
0	.717(-10)	.687(-10)	.509(-10)	.436(-10)	.317(-10)	.203(-10)
1	.115(-09)	.934(-10)	.800(-10)	.582(-10)	.492(-10)	.285(-10)
2	.116(-09)	.135(-09)	.116(-09)	.912(-10)	.703(-10)	.438(-10)
3	.462(-10)	.183(-09)	.152(-09)	.122(-09)	.948(-10)	.558(-10)
4	.130(-10)	.151(-09)	.198(-09)	.156(-09)	.122(-09)	.699(-10)
5	.396(-11)	.655(-10)	.215(-09)	.208(-09)	.168(-09)	.925(-10)
6	.105(-11)	.238(-10)	.186(-09)	.232(-09)	.214(-09)	.122(-09)
7	.547(-12)	.915(-11)	.835(-10)	.248(-09)	.243(-09)	.161(-09)
8	.612(-13)	.246(-11)	.324(-10)	.209(-09)	.261(-09)	.196(-09)
9	.291(-13)	.100(-11)	.125(-10)	.106(-09)	.209(-09)	.217(-09)
10	.280(-13)	.125(-12)	.507(-11)	.447(-10)	.102(-09)	.230(-09)
11	.000(-00)	.174(-12)	.159(-11)	.206(-10)	.489(-10)	.210(-09)
12	.299(-13)	.888(-13)	.693(-12)	.493(-11)	.151(-10)	.927(-10)
13		.316(-13)	.200(-12)	.121(-11)	.381(-11)	.299(-10)
14				.202(-12)	.106(-11)	.462(-11)

Table 5   H + H_2 LSTH REACTIVE T=4000 K

4.1.2   The Li + HF reaction

In the realm of three-atom systems, the prototypal role of truly A + BC asymmetric reactions is played by Li + HF → LiF + H. After the early CMB investigation of Lee and coworkers (99) in more recent years further experiments have been carried out involving also HF vibrational excitation and orientation (100; 101). For this system extensive *ab initio* calculations have been reported in ref. (102) and further calculations have been discussed in ref. (103). On these ab initio values a PES was fit whose parameters, functional formulations and results obtained from dynamical calculations are discussed in

refs. (104; 105; 106). Here, we plot in figure 1 the QM reactive probability calculated at $\nu = 0$ and $j = 0$ at different values of the total angular momentum quantum number J. Similar calculations performed on a different PES are given in refs. (107; 108; 109). The situation for this system, as is for many other atom-diatom and, *a fortiori*, for the diatom-diatom systems we discuss in the followings, is still that of assessing the accuracy of the proposed PESs.
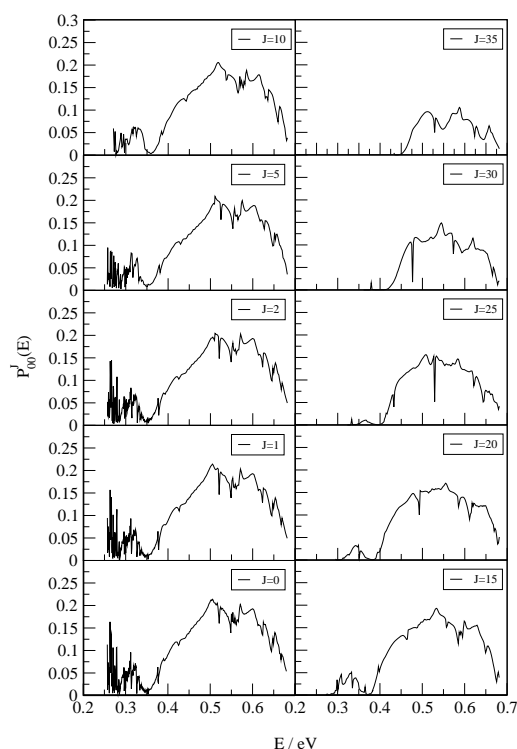

Figure 1: QM reaction probabilities calculated for the Li + FH reaction at $\nu = 0$ and $j = 0$ for different values of the total angular momentum quantum number J plotted as a function of the total energy E.

4.2   Polyatomic reactions

Reactions involving more than three-atoms can be divided into two classes: atom polyatomic molecules processes and free radicals (diatomic or polyatomic) molecules (diatomic or polyatomic) ones. While there has been a number of CMB studies of atom-polyatomic molecule reactions much fewer have been those concerned with free radical molecule reactions.

In the past, reactive DCS for radical-molecule reactions have been measured using effusive beams of CH_3 and OH radicals (110; 111; 112) and using mildly supersonic CH_3 beams generated by pyrolysis (113; 114). More recently, DCS radical-molecule reactions have been measured for reactions of OH (with H_2 and CO) and CN (with H_2) by mass

spectrometric/TOF and Doppler selected/TOF detection, respectively. ICS resolved over the final products states were also determined for CH (17) NH, NH_2 (115) and CN (116) using laser spectroscopy probing the collision region. CMB studies were also carried out for CN reactions with unsaturated hydrocarbons and polyatomic radical (C_2D, C_3H_3, C_6H_5).

4.2.1 The OH + H_2 reaction

The development of a continuous, intense supersonic beam of OH radicals has been the key to the first successful measurement of product angular and velocity distributions for the OH + $H_2 \rightarrow H_2O$ + H reaction

DCS of the $^{18}OH + D_2$ reaction were measured by Casavecchia and collaborators (118; 119) using a crossed beam apparatus to detect the HOD product. The product *cm* angular and translational energy distributions obtained from the experiment were measured at a collision energy of 6.3 kcal/mol. The experiment indicates that the angular distribution of the HOD product is strongly backward (with respect to the OH incoming direction). The authors attributed this to the rebound nature of the reactive mechanism. They also found that the average fraction of energy available as translation of the products is only 0.32 and that, accordingly, the percentage of internal energy is high. More recently, Daris and coworkes have obtained vibrationally resolved DCS for the same reaction by using the H-atom Rydberg tagging techniche citecasa-science. Experimental kinetic studies of this reaction have also been performed (121; 122; 123; 124; 125; 126).
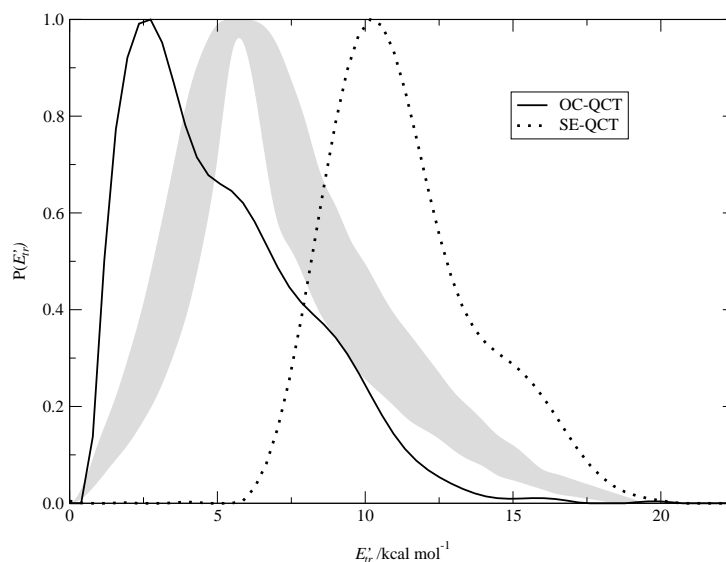

Figure 2: Product translational distribution for the $^{18}OH + D_2 \rightarrow H^{18}OD$ + D reaction evaluated at E_{tr}=6.3 kcal/mol. Experimental values from ref. (119) are given as a shaded area, QCT values calculated on the OC PES are given as a dashed line and QCT values calculated on the SE PES are given as a dashed-dotted line.

Here, results of highly converged QCT calculations are compared with the experimental data (118; 119). The PES mostly widely used for dynamical calculations of the reactive

properties of the OH + H$_2$ system is the one proposed by Schatz and Elgersma (SE) (127) which is based on the *ab initio* calculations of Walch and Dunning (128). The SE PES adopts an MBE (Many-Body Expansion) formulation of the interaction and expresses the two body terms as Morse functions, the three body terms as LEPS and quadratic Sorbie Murrell functionals, and the four body term as a sum of two exponentials of polynomials of the related internuclear distances.

A more recent fit of the PES (129) based to the *ab initio* energies of Werner and coworkers was also performed using an extension to four atoms of the LAGROBO (Largest Angle Generalization of ROtating Bond Order) many process functional representation of the interaction (130; 131; 132) by Ochoa and Clary (OC).

CMB results of the ^{18}OH + D$_2$ → H^{18}OD + D reaction allow a comparison of calculated *cm* product translational energy (PTD) distributions obtained by plotting the reactive probability $P(E'_{tr})$ as a function of E'_{tr} with measured data. To this end half million trajectories were integrated on both the SE and the OC PESs at $E_{tr} = 6.3$ kcal/mol, $\nu = 0$, $j_{OH} = 0$ and $j_{D_2} = 2$ to mimic experimental conditions (119). The different properties of the two PESs show up clearly in the PTD structures plotted in Fig. 2. The PTD calculated on the OC PES has, in fact, its maximum at $E'_{tr} = 3$ kcal/mol (dashed line) while the one calculated on the SE PES has its maximum at $E'_{tr} = 11$ kcal/mol (dashed dotted line). As apparent from the figure the measured distribution (given as the dashed area of the experimental error bars) has an intermediate position with the maximum located at $E'_{tr} = 5.5$ kcal/mol (2.5 kcal/mol above that of OC results and 5.5 kcal/mol below that of the SE ones). Other differences between calculated and experimental properties are the lower value of the theoretical cross sections (with respect to the measured ones). This means that also the OC PES is still far from having the accuracy necessary for use in rigorous dynamical calculations. As a matter of fact new ab initio calculations have been performed and their fit based on a Shepard intepolation has been proposed (133). Though the new surface does not seems yet to behave properly in the long range region it marks a definite improvement over the previous ones and therefore deserves to be tested by running massive trajectory calculations.

4.2.2 The OH + CO reaction

Extensive experimental investigations (134; 135; 136; 137; 138; 139; 140; 141; 142; 143; 144; 23; 22; 145; 146; 147; 148) have been carried out for the OH + CO → H + CO$_2$ reaction. As to theory, also several calculations (149; 150; 151; 152; 153; 154; 155; 156; 157; 158; 159; 160; 161; 162; 163; 164; 165) have been carried out. Calculations and experiments have also been carried out for the reverse H + CO$_2$ → OH + CO reaction (166; 167; 168; 169; 170; 171; 172; 173; 174) as well as for related isotopic variants. Previous work is reviewed in ref. (117) and a great deal of research is still reported on these systems at the top international conferences in the field (see for recent examples refs. (175; 176)).

The first full-dimensional PES for the OH + CO system based on the many-body expansion approach (177) was proposed by Schatz and coworkers (166). The two and three body terms consist of polynomials in the related internuclear distances multiplied by damping functions to make the potentials vanish at large distances. The four body term consists of products of polynomials (of the same kind used for the two and three

body terms) and Gaussians enforcing the reproduction of the ab initio stationary points. Subsequently the PES was further improved (149; 167) in order to better reproduce the ab initio calculations of ref. (166) and to smooth out singularities occurring during the numerical evaluation of the potential energy and its derivatives.

Recently, using the potential energy values obtained from a new set of ab initio calculations, a more accurate evaluation of the stationary points of the surface was carried out and a new fit (YMS) was performed (178; 179; 180). More recently, the PES of Schatz and coworkers was also further modified (159) and the new PES (LTSH) is in better agreement with the most recent ab initio values and avoids some of the singularities occurring during the calculation of the derivatives. To this end the parameters of the four body term and the coefficients of the long range part of the OH + CO entrance channel were optimized to reproduce the ab initio values of refs. (178; 179; 180). To study the influence on the dynamics of the wells located in the reactant channel also a modified version of the LTSH PES (called mod-LTSH) was produced (165) by suppressing the long range tail of the surface in the reactant channel.

To work out a theoretical estimate of the PTD at the conditions of the experiment, we performed QCT calculations on both the YMS and LTSH PESs by setting the collision energy at 8.6 and 14.1 kcal mol^{-1} and the vibrational energy of both the OH and CO molecules at that of their ground rovibrational state. Batches of more than one million trajectories were run using a maximum impact parameter of 2.6 and 2.4 Å for the YMS and the LTSH PESs respectively and accepting only trajectories conserving total energy to better than 4×10^{-2} kcal/mol.

The PTDs calculated on the YMS PES have a location of the maximum depending on the reactant collision energy (that is at $E'_{\mathrm{tr}} = 19$ and 21 kcal mol^{-1} for reactant collision energies of 8.6 and 14.1 kcal mol^{-1}, respectively). On the contrary the PTDs calculated on the LTSH PES at the same collision energies have both maxima at $E'_{\mathrm{tr}} = 23$ kcal mol^{-1}. The PTDs are basically symmetric (the average product translational energies is coincident with the value at the maxima) with the distributions calculated at $E_{\mathrm{tr}} = 14.1$ kcal mol^{-1} being slightly broader than the ones calculated at $E_{\mathrm{tr}} = 8.6$ kcal mol^{-1}. An even more dramatic difference between the two sets of PTDs is that those calculated on the LTSH PES are systematically closer to the experimental distribution than those calculated on the YMS one. However, none of the calculated PTDs coincides with the experimental one.

These results and the need for rejecting a large fraction of trajectories not conserving total energy within the imposed boundaries are a clear indication that the proposed PESs are still too far from the quality standards required for carrying out dynamical calculations.

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